(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 201 871**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86106297.4

(51) Int. Cl.⁴: C07C 43/12 , C07C 41/06

(22) Date of filing: 07.05.86

(30) Priority: 17.05.85 IT 2078185

(43) Date of publication of application:
20.11.86 Bulletin 86/47

(84) Designated Contracting States:
AT BE CH DE FR GB LI NL SE

(71) Applicant: AUSIMONT S.p.A.
31, Foro Buonaparte
I-20121 Milano(IT)

(72) Inventor: Guglielmo, Giorgio
Via A.Gramsci 89
I-30035 Mirano/Venezia(IT)
Inventor: Gambaretto, Giampaolo
7, via Torino
I-35142 Padova(IT)

(74) Representative: Jaumann, Paolo
Studio Consulenza Brevetti Jaumann Piazza Castello, 2
I-20121-Milano(IT)

(54) Fluoro-halo-ethers and process to produce them.

(57) Flouro-halo-ethers of general formula:

$(R)_nC(F)_m$-O-CAF-CAF_2

wherein R is a partly or completely halogenated hydrocarbon, alkyl monoether or alkyl polyether radical, A is either chlorine or bromine, n is an integer selected between 1 and 2, m is an integer equal to 3-in. The value n = 2 comprises the compounds wherein C is a part of a cyclic ring.

EP 0 201 871 A1

"FLOURO-HALO-ETHERS AND PROCESS TO PRODUCE THEM"

Background of the Invention

1. Field of the Invention

The present invention relates to flouro-halo-ethers and to the process to obtain them.

More particularly, the present invention relates to flouro-halo-ethers suitable to be dehalogenated to the purpose of forming the corresponding flouro-halogenated vinyl ethers and to the related process to obtain them.

2. Description of the Prior Art

From the tecnical literature some types of flouro-halo-ethers are hnown, which are advantageously used as hypnotic or anaesthetic agents, and in the phytosanitary and phytopharmaceutical field.

These fluoro-halo-ethers of the prior are are characterized in that both the radicals bonded to the oxygen atom contain hydrogen.

U.S. Patents Nos. 3,557,294; 3,897,502; 3,784,706; 3,764,706; 3,947,595; 3,976,788; 3,943,256; 3,987,111; 4,357,282 disclose these flouro-halo-ethers and the process for preparing them.

U.S. PATENT No.4,334,105 discloses a particular type of halo-ethers, the characteristic of which is that of having only one reducible group "CZ_2" on at least one of the radicals bonded to the oxygen atom. According to said patent, such characteristic of reducibility is achieved when "Z" is either bromine or chlorine, or both of them.

The presence of only one reducible group on each radical does not allow the corresponding vinyl-ethers to be obtained by simple dehalogenating.

The French Patent No. 2,287,432 discloses some fluorinated mono-and di-ethers, which, in the case of monoethers, correspond to the general formula:

$$F\text{-}R_f\text{-}CF_2\text{-}O\text{-}R\text{-}H$$

wherein R_f is a perflourinated aliphatic chain and R is a possibly substituted aliphatic radical.

Also these fluoro-ethers are however unsuitable to undergo a dehalogenating reaction leading to the formation of fluoro-halogenated vinyl-ethers.

The Present Invention

Purpose of the present invention is to provide new fluoro-halo-ethers suitable to be dehalogenated to the purpose of forming the corresponding vinyl-ethers.

Further purpose of the present invention is to provide a process for the preparation of fluoro-halo-ethers suitable to be dehalogenated to the purpose of forming the corresponding vinyl-ethers.

It has now been surpisingly found by the present Applicant and this is one object of the present invention, that these purposes are achieved by means of new fluroro-halo-ethers of general formula:

$$(R)_nC(F)_m\text{-}O\text{-}CAF\text{-}CAF_2 \quad (I)$$

wherein A is selected from chlorine and bromine, R is an alkyl, cycloalkyl, aromatic, alkyl monoether or alkyl polyether radical containing from 1 to 20 carbon atoms, partly or completely halogenated with bromine, chlorine, iodine and/or flourine as substituents, n is an integer selected from 1 and 2, m is an integer equal to 3-n, it being intended that the value n = 2 comprises the compounds in which C is part of a cyclic ring.

In the present invention the fluoro-halo-ethers of general formula (I) wherein A is chlorine and R is either a perhaloalkyl radical containing from 1 to 5 carbon atoms and halogens of the type of fluorine, chlorine and/or bromine, or a perfluoroalkyl monoether containing from 1 to 5 carbon atoms, are preferred.

Examples of fluoro-halo-ethers being the object of the present invention are those having the following formulae:

$CF_3\text{-}CF_2\text{-}CF_2\text{-}O\text{-}CClF\text{-}CClF_2$

$CF_3\text{-}CF_2\text{-}O\text{-}CClF\text{-}CClF_2$

$CClF_2\text{-}CF_2\text{-}O\text{-}CClF\text{-}CClF_2$

$CCl_2F\text{-}CF_2\text{-}O\text{-}CClF\text{-}CClF_2$

$CCl_3\text{-}CF_2\text{-}O\text{-}CClF\text{-}CClF_2$

$CBrF_2$-CF_2-O-CClF-$CClF_2$

CF_3-O-CF_2CF_2-O-CClF-$CClF_2$

C_2F_5-O-CF_2CF_2-O-CClF-$CClF_2$

$(CF_3)_2$CF-O-CClF-$CClF_2$

The fluoro-halo-ethers being the object of the present invention have never been described in the technical literature and have the characteristic that both their groups -CAF-are reducible. This characteristic allows the corresponding fluoro-halogenated vinyl-ethers to be obtained by dehalogenation.

According to another aspect of the present invention, the products of formula (I) can be obtained by a synthesis route starting from a fluoro-oxy-halo compound and a halo-olefin according to the reaction scheme:

$$\underset{(II)}{(R)_nC(F)_m-O-F} + \underset{(III)}{CAF=CAF} \longrightarrow \underset{(I)}{(R)_nC(F)_m-O-CAF-CAF_2}$$

wherein A, R, n and m have the same meaning as described hereinabove.

The fluoro-oxy-halo compound having formula:

$(R)_nC(F)_m$ -O-F (II)

can be obtained according to any known process, and in particular according to the process disclosed in Italian Patent Application No.19,847 A/85.

The compounds being the object of the present invention, having the general formula (I), can be obtained by reacting the fluoro-oxy-halo compound with the halogenated olefin, for example in the gas phase, under atmosphereric or slightly superatmospheric pressure, such as, e.g., up to 5 atmospheres, at a temperature comprised within the range of from -80°C to 50°C.

The reaction can be carried out by feeding the reactants as such, or diluted by inert gases or vapours, such as, e.g., N_2, He, CF_4, $CClF_3$, CCl_2F_2, $CHClF_2$, C_2ClF_5, $C_2Cl_2F_4$.

In the process being object of the present invention, concentrations of the sum of the reactants comprised within the range of from 1 to 50% by volume are preferred.

Examples illustrative compounds having general formula (II) which can be used in the process being one object of the present invention comprises:

fluorooxy-pentafluoro-ethane; fluorooxy-2-chloro-tetra-fluoro-ethane; fluorooxy-2,2-dichloro-trifluoro-ethane; fluorooxy-2,2,2-trichloro-difluoro-ethane; fluorooxy-2-bromo-tetrafluoro-ethane; fluorooxy-heptafluoro-propane; fluorooxy-perfluoro-butane; perfluoroethoxy-perfluoroethylhyopfluorite; perfluoromethoxy-perfluoroethyl-hypofluorite and their mixtures; perfluoroisopropylhypofluorite, and so forth.

In the process being object of the present invention any halogenated olefin of general formula (III) can be used, on condition that both its groups -CAF-are reducible. Illustrative examples of preferred halogenated olefins are: 1,2-difluoro-dichloro-ethylene, 1,2-difluoro-dobromo-ethylene, 1-chloro-2-bromo-difluoro-ethylene, and so forth.

To the purpose of better understanding the present invention and to show practical embodiments thereof, hereunder some illustrative but not limitative Examples are reported.

Example 1

To the top of a metal tubular reactor of 1 cm of inner diameter and of 1300 cm of length, cooled at -30°C, an N_2/C_2F_5OF gas mixture at 20% by volume of C_2F_5OF is fed under an absolute pressure of 110 kPa; at a distance of about 300 cm from the top a C_2ClF_5/CClF = CClF gas mixture of 20% by volume of CClF = CClF is fed. The flow rate of the two streams is adjusted at 18.7 Nl/h each. The stream leaving the reactor is cooled to -80°C and the condensate is distilled.

After 6 hours of continuous feeding, 72 g is obtained of a fraction at 99% by weight of C_2F_5OC ClF-$CClF_2$. Yield 25% by mol.

The product is identified by mass spectrophotometry and has a boiling point of 60-62°C.

A sample of the so obtained product has been submitted to a dechlorination process by zinc dimethylsulphoxide at 40°C, with a yield higher than 90%. The corresponding fluorovinylether

$C_2F_5OCF=CF_2$

Obtained has a boiling point of 9°C.

Example 2

The test is carried out as in Example 1, but feeding at the reactor top an $N_2/CClF_2$-CF_2OF gas mixture at 20% by volume of $CClF_2$-CF_2OF.

After 10 hours of continuous feeding and subsequent distillation, 31 g is obtained of product at 99%, which by mass spectrophotometric analysis has been identified as

$CClF_2$-CF_2-O-CClF-$CClF_2$;

the product shows a boiling point of 90-92°C.

Example 3

The test is carried out as in Example 1, but feeding at the reactor top an N_2/CF_3-CF_2-CF_2-OF gas mixture at 20% by volume of CF_3-CF_2-CF_2-OF.

After 10 hours of continuous feeding and subsequent distillation. 40 g is obtained of product at 99%, which by mass spectrophotometric analysis has been identified as

CF_3-CF_2-CF_2-O-CClF-$CClF_2$.

Claims

1. Fluoro-halo-ethers of general formula:

$(R)_nC(F)_m$-O-CAF-CAF_2

wherein A is selected from chlorine and bromine, R is an alkyl, cycloalkyl, aromatic, alkyl monoether or alkyl polyether radical containing from 1 to 20 carbon atoms, partly or completely halogenated with bromine, chlorine, iodine and/or fluorine as substituents, n is an integer selected from 1 and 2, m is an integer equal to 3-n, wherein the value n = 2 comprises the compounds in which C is part of a cyclic ring.

2. Flouro-halo-ethers according to claim 1, wherein R is a perhaloalkyl radical containing from 1 to 5 carbon atoms.

3. Fluoro-halo-ethers according to claim 2, wherein the perhaloalkyl radical contains halogens of the type of fluorine, chlorine and/or bromine.

4. Fluoro-halo-ethers according to claim 1, wherein R is a perfluoroalkyl monoether radical containing from 1 to 5 carbon atoms.

5. Fluoro-halo-ether according to any of foregoing claims, wherein A is chlorine.

6. Fluoro-halo-ether according to claim 1, of formula:

CF_3-CF_2-O-CClF-$CClF_2$

7. Fluoro-halo-ether according to claim 1, of formula:

$CClF_2$-CF_2-O-CClF-$CClF_2$

8. Fuoro-halo-ether according to claim 1 of formula:

CCl_2F-CF_2-O-CClF-$CClF_2$

9. Fluoro-halo-ether according to claim 1, of formula:

CCl_3-CF_2-O-CClF-$CClF_2$

10. Fluoro-halo-ether according to claim 1, of formula:

$CBrF_2$-CF_2-O-CClF-$CClF_2$

11. Fluoro-halo-ether according to claim 1, of formula:

CF_3-O-CF_2CF_2-O-CClF-$CClF_2$

12. Fluoro-halo-ether according to claim 1, of formula:

C_2F_5-O-CF_2CF_2-O-CClF-$CClF_2$

13. Fluoro-halo-ether according to claim 1, of formula:

$(CF_3)_2$CF-O-CClF-$CClF_2$

14. Fluoro-halo-ether according to claim 1 of formula:

$CF_3CF_2CF_2$-O-CClF-$CClF_2$

15. Process for the preparation of the fluoro-haloethers according to any of foregoing claims, consisting in reacting a fluoro-oxy-halo compound with a halogenated olefin according to the scheme:

$$(R)_nC(F)_m-O-F + CAF=CAF \longrightarrow (R)_nC(F)_m-O-CAF-CAF_2$$

wherein A, R, n and m have the hereinabove reported meaning.

European Patent Office

EUROPEAN SEARCH REPORT

. Application number

EP 86106297.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	US - A - 4 334 105 (ROSS C. TERRELL et al.) * Claim 1 * --	1-3	C 07 C 43/12 C 07 C 41/06
A	US - A - 3 558 721 (CHARLES CHENG-YU YAO) * Claim 1 * --	1-3	
A	DE - A1 - 3 438 934 (OCCIDENTAL CHEMICAL CORP.) * Claims 1,3 * ----	1,15	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 C 43/00
C 07 C 41/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	01-07-1986	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03 82